

Temperature and composition phase diagram in the iron-based ladder compounds



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We investigated the iron-based ladder compounds $(\text{Ba,Cs})\text{Fe}_2\text{Se}_3$. Their parent compounds, BaFe_2Se_3 and CsFe_2Se_3 , have different space groups, formal valences of Fe and magnetic structures. Electrical resistivity, specific heat, magnetic susceptibility, X-ray diffraction and powder neutron diffraction measurements were conducted to obtain temperature and composition phase diagram of this system. Block magnetism observed in BaFe_2Se_3 is drastically suppressed with Cs doping. In contrast, stripe magnetism observed in CsFe_2Se_3 is not so fragile against Ba doping. New type of magnetic structure appears in intermediate compositions, which is similar to stripe magnetism of CsFe_2Se_3 , but inter-ladder spin configuration is different. Intermediate compounds show insulating behavior, nevertheless finite T -linear contribution in specific heat was obtained at low temperatures.

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I. INTRODUCTION

Iron-based superconductors (SCs) have created considerable interests in condensed matter physics community since its discovery [1]. Despite intensive efforts, the superconducting mechanism is still controversial; spin fluctuation [2], orbital fluctuation [3], or both of them are prime candidates for mechanism of the iron-based SCs. As these fluctuations are sensitive to crystal and magnetic structure, it is desired to explore superconductivity in iron-based compounds with different crystal and magnetic structures.

To date iron-based SCs are known to have the two dimensional Fe square lattice with Fe atoms being tetrahedrally coordinated by pnictogens or chalcogens. They show metallic behavior in electrical resistivity, and have antiferromagnetic order [4, 5]. The 1111 [6, 7], 111 [8, 9] and 122 [10, 11] systems have single-stripe magnetic structure and their magnetic moments are less than $1 \mu_B$. The 11 systems have double stripe magnetic structure with $\sim 2 \mu_B$ moment [12, 13]. In contrast, the 245 systems, $\text{A}_2\text{Fe}_4\text{Se}_5$ ($A = \text{K, Rb, and Cs}$), are insulators and have two-dimensional (2D) iron square lattice with periodic vacancy of Fe atoms [14, 15]. They have block magnetism with magnetic moments $\sim 3 \mu_B$ and have been considered to be the third type of magnetic structures for parent compounds of iron-based SCs.

To gain further insights into the interplay between crystal structure, magnetism and superconductivity, research on compounds with different dimensionality is important. The spatial dimensionality should have effects on magnetic interaction, orbital selectivity and topology of Fermi-surface of Fe atoms. In this regard, it is noteworthy that one-dimensional spin-ladder systems ($\text{La, Y, Sr, Ca})_{14}\text{Cu}_{24}\text{O}_{41}$ provide great insight into the understanding of the two-dimensional copper-oxide superconductors [16].

Recently, iron-based ladder compounds AFe_2X_3 ($A = \text{K, Rb, Cs or Ba, and } X = \text{chalcogen}$) [17–19] have been under intensive investigation [20–28]. The AFe_2X_3 compounds consist of FeX_4 tetrahedra, which is similar to the 2D iron-based SCs, but Fe atoms form two-leg ladder lattice giving rise to the quasi-one dimensionality. They also show related magnetism with iron-based SCs, stripe and block magnetism. Unlike the most iron-based SCs, iron-based ladder compounds are insulators. KFe_2Se_3 [26] and CsFe_2Se_3 [25] have stripe magnetism; magnetic moments are arranged to form ferromagnetic units along the rung direction, and the units stack antiferromagnetically along the leg direction. BaFe_2Se_3 [20, 23] has block magnetism; magnetic moments are arranged to form Fe_4 ferromagnetic units, and each units stack antiferromagnetically along the leg direction. Interestingly, in BaFe_2Se_3 , Fe lattice distortion under Néel temperature (T_N) is reported

[20, 23]. This indicates that lattice and magnetism are strongly coupled.

Recently magnetization measurement for the iron-based ladder compounds $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{Se}_3$ have been reported [26]. BaFe_2Se_3 has the $Pnma$ space group, formal valence of Fe^{2+} and block magnetism with $T_N \sim 255$ K [20, 23]; on the other hand KFe_2Se_3 has the $Cmcm$ space group, formal valence of $\text{Fe}^{2.5+}$ and stripe magnetism with $T_N \sim 200$ K [26]. The previous study determined T_N of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{Se}_3$ from magnetization measurement and showed reduced T_N by K doping decreases [26]. However, little is known on the variation of the crystal and magnetic structures in intermediate compositions.

In this study, we focus on the mixed system of BaFe_2Se_3 and CsFe_2Se_3 . CsFe_2Se_3 has the $Cmcm$ space group, formal valence of $\text{Fe}^{2.5+}$, stripe magnetism similar to KFe_2Se_3 with $T_N \sim 175$ K [25]. Since CsFe_2Se_3 has lower T_N than KFe_2Se_3 , we assumed that T_N was strongly suppressed by dilution. We examined $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ through electrical resistivity, specific heat, magnetic susceptibility, X-ray diffraction and powder neutron diffraction measurements, and established composition and temperature phase diagram of $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$. The boundary of the two distinct space groups, $Pnma$ and $Cmcm$, is between $x = 0.05$ and 0.15 . Block magnetism in BaFe_2Se_3 is drastically suppressed by Cs doping, whereas stripe magnetism in CsFe_2Se_3 is relatively stable. In addition, new magnetic structure is observed for $x = 0.5, 0.55$ and 0.65 at the lowest temperatures. Surprisingly at $x = 0.25$, no magnetic reflections were observed down to 7 K in the powder neutron diffraction.

II. EXPERIMENTAL

Polycrystalline samples of $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ ($x = 0.05, 0.15, 0.25, 0.4, 0.5, 0.55, 0.65$ and 0.75) were synthesized from the mixture of BaFe_2Se_3 and CsFe_2Se_3 . The values of x were defined as nominal composition. The two parent compounds were synthesized from the stoichiometric ratio of the starting materials such as $\text{Ba} : \text{Fe} : \text{Se} = 1 : 2 : 3$ and $\text{Cs}_2\text{Se} : \text{Fe} : \text{Se} = 1 : 4 : 5$ [20, 25]. They were mixed in a carbon crucible sealed into a quartz tube with 0.3 atm of Ar gas and reacted at 900 °C for 24 hours.

Single crystals of $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ ($x = 0.05, 0.15, 0.25, 0.4, 0.5, 0.55, 0.65$ and 0.75) were grown from the melt. Stoichiometric mixtures of the two parent compounds were put in a carbon crucible and then sealed into a quartz tube with 0.3 atm of Ar gas. They were reacted at 1100 °C for 24 hours and cooled to 750 °C with a rate of 6 °C/h, and then cooled down to room temperature for 12 hours. Reflecting one dimensionality of the structure, the crystals preferentially grew along the leg direction.

Quality of the samples was checked by the powder x-ray diffraction (XRD) with $\text{Cu-K}\alpha$ radiation at room temperature. No detectable amount of impurities were

TABLE I. Detailed diffractometer parameters. Samples are packed into vanadium cans. Temperature is controlled by using a Closed-cycle refrigerator (CCR).

Diffractometer	ECHIDNA	WAND
Wave length (Å)	2.4395(2)	1.4827(1)
2θ range (deg.)	2.75-163.875	5.025-129.625
2θ step (deg.)	0.125	0.2
Monochromator	Ge(335)	Ge(113)
Refrigerator	CCR (3-300 K)	CCR (5-300 K)

observed in the XRD measurements. Single-crystal XRD with $\text{Mo-K}\alpha$ radiation was performed by using R-Axis RAPID II (Rigaku) at room temperature to determine the space group of $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$.

Electrical resistivity is measured using the four-probe method in the temperature (T) range between 30 and 300 K. Specific heat measurements were performed using relaxation method between $T = 1.8$ and 300 K. These measurements were performed using the Physical Properties Measurement System (Quantum Design, PPMS).

DC susceptibility was measured between $T = 2$ and 300 K under magnetic field up to $H = 5$ T using a commercial SQUID magnetometer (Quantum Design, MPMS).

Powder neutron diffraction was performed using the high-resolution ECHIDNA diffractometer at the Australian Nuclear Science and Technology Organization, and the Wide-Angle Neutron Diffractometer (WAND) at Oak Ridge National Laboratory. Experimental conditions are summarized in Table I. The Rietveld refinements were performed using the Fullprof suite [29]. The crystal structures were depicted by the VESTA software [30].

III. RESULTS

A. CRYSTAL STRUCTURE

Figure 1 shows neutron diffraction patterns for $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ together with Rietveld refinement results at 300 K.

Table II summarizes refined atomic positions, and other crystallographic data from the Rietveld refinement are shown in Table III. A little amount of carbon contamination was found for $x = 0.65$ and 0.75 samples, 0.55(1) % and 0.027(1) % weight ratio, respectively. In addition, an unindexed impurity phase was detected for $x = 0.75$ sample, with the strongest peak which is roughly 20 times smaller than the main phase. Although their peak intensities are very weak, they could affect the refinement results. Hence, we excluded these 2θ regions: 41.9-43.2° (carbon) for $x = 0.65$, and 24.5-25.3°, 47.8-48.7° (unknown impurity) and 42.2-42.9° (carbon) for $x = 0.75$ during the refinements.

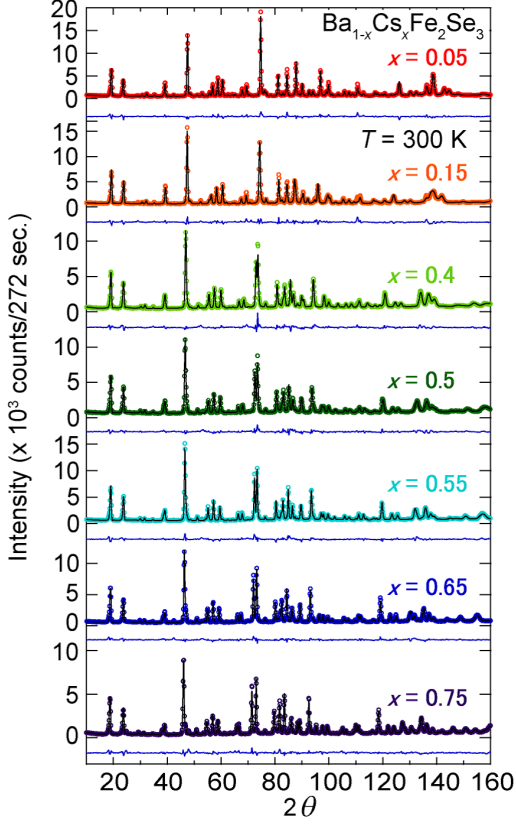


FIG. 1. (color online). High-resolution powder neutron diffraction patterns of $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ at 300 K on ECHIDNA together with Rietveld analysis. The bottom blue lines give the difference between the observed (open circles) and calculated (line) intensities.

The space group of $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ was determined using single crystal XRD. We assumed that $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ belong to either $Pnma$ or $Cmcm$, and that the structure boundary should exist between $x = 0$ and 1. It should be noted that the presence of 112_{Pnma} nuclear reflection, which is forbidden in the $Cmcm$, was used to determine the space group of $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$. We found that the 112_{Pnma} reflection was present for $x = 0.05$, but absent for $x \geq 0.15$ in the rotation photographs taken at the room temperature. It is reported that BaFe_2Se_3 undergoes a phase transition from the $Pnma$ to $Cmcm$ structure at 660 K [21]. Accordingly, it is natural to consider that the boundary of $Pnma$ and $Cmcm$ crosses 300 K between $x = 0.05$ and 0.15.

Figure 2(a) shows the crystal structure of $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$, and Fig. 2(b) depicts one Fe ladder with both notation of $Pnma$ and $Cmcm$. Figures 2(c) and 2(d) provide view being parallel to the leg direction of $Cmcm$ and $Pnma$ structure, respectively. The Fe ladders slightly incline in the $Pnma$ structure. Since the definitions of a, b and c axes in $Pnma$ and $Cmcm$ are different, hereafter in this paper, the axes of $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ are defined as follows: the a axis is

TABLE II. Refined atomic positions at 300 K for $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ ($x = 0.05, 0.15, 0.4, 0.5, 0.55, 0.65$, and 0.75). Note that $x = 0.05$ belongs to the $Pnma$ space group. The others belong to $Cmcm$.

Atom	site	x	y	z	$U_{\text{iso}} (\text{\AA}^2)$
$x = 0.05$					
Ba/Cs	4c	0.1798(8)	1/4	0.508(2)	0.020(3)
Fe	8d	0.4960(4)	0.0008(10)	0.3544(4)	0.0120(9)
Se1	4c	0.3632(6)	1/4	0.2265(8)	0.022(3)
Se2	4c	0.6281(6)	1/4	0.4959(11)	0.0131(19)
Se3	4c	0.3938(6)	1/4	0.8100(7)	0.007(2)
$x = 0.15$					
Ba/Cs	4c	1/2	0.1788(8)	1/4	0.011(3)
Fe	8e	0.3518(5)	1/2	0	0.0223(11)
Se1	4c	0	0.1245(6)	1/4	0.011(2)
Se2	8g	0.2073(6)	0.3804(5)	1/4	0.040(2)
$x = 0.4$					
Ba/Cs	4c	1/2	0.1725(8)	1/4	0.025(3)
Fe	8e	0.3527(5)	1/2	0	0.0185(10)
Se1	4c	0	0.1215(5)	1/4	0.0099(19)
Se2	8g	0.2120(5)	0.3818(5)	1/4	0.0429(19)
$x = 0.5$					
Ba/Cs	4c	1/2	0.1732(7)	1/4	0.023(3)
Fe	8e	0.3540(5)	1/2	0	0.0247(10)
Se1	4c	0	0.1195(5)	1/4	0.0163(19)
Se2	8g	0.2153(5)	0.3833(5)	1/4	0.0467(19)
$x = 0.55$					
Ba/Cs	4c	1/2	0.1720(7)	1/4	0.028(3)
Fe	8e	0.3539(4)	1/2	0	0.0286(10)
Se1	4c	0	0.1209(5)	1/4	0.0149(17)
Se2	8g	0.2177(5)	0.3837(5)	1/4	0.0522(19)
$x = 0.65$					
Ba/Cs	4c	1/2	0.1729(6)	1/4	0.028(2)
Fe	8e	0.3552(4)	1/2	0	0.0214(8)
Se1	4c	0	0.1200(4)	1/4	0.0175(15)
Se2	8g	0.2180(4)	0.3840(4)	1/4	0.0404(14)
$x = 0.75$					
Ba/Cs	4c	1/2	0.1714(7)	1/4	0.031(2)
Fe	8e	0.3563(3)	1/2	0	0.0123(8)
Se1	4c	0	0.1205(4)	1/4	0.0103(16)
Se2	8g	0.2208(4)	0.3867(3)	1/4	0.0244(13)

along the rung direction, the b axis is perpendicular to the two-leg ladder plane, and the c axis is along the leg direction, which is indeed the axis choice of the $Cmcm$ space group. Figure 3(a) shows x dependence of lattice constants a, b and c . Among the three lattice constants, the b value significantly deviates from the linearity in $0 < x < 0.5$. In particular for $x = 0.15$ roughly 2 % deviation was found. It should be noted that this composition is close to the structural transition from the $Pnma$ to the $Cmcm$. We also note that the decrease of the b value indicates reduction of inter-ladder distance, giving rise to enhanced three dimensionality. Figure 3(b) shows that x dependence of local structure parameters at 300 K. The definition of the local structure parameters are given in Fig. 2(b); the leg, rung, L indicate the Fe-Fe bond lengths; α_1 and α_2 are the Se-Fe-Se bond angles. Local structures change continuously in $x \leq 0.15$ region,

TABLE III. Refined crystallographic data taken at 300 K. Chemical formula units Z is 4 for all x . Excluded regions contain peaks from carbon ($2\theta = 41.9\text{--}43.2^\circ$ for $x = 0.65$ and $42.2\text{--}42.9^\circ$ for $x = 0.75$), and unknown impurity ($2\theta = 24.5\text{--}25.3^\circ$ and $47.8\text{--}48.7^\circ$ for $x = 0.75$). $R_p = \sum_i |y_{\text{obs}} - y_{\text{calc}}| / \sum_i y_{\text{obs}}$; $R_{wp} = [\sum_i w_i |y_{\text{obs}} - y_{\text{calc}}|^2 / \sum_i w_i y_{\text{obs}}^2]^{1/2}$.

Formula	$x = 0.05$	$x = 0.15$	$x = 0.4$	$x = 0.5$	$x = 0.55$	$x = 0.65$	$x = 0.75$
Molar mass (g/mol)	485.7	485.2	484.1	483.7	483.5	483.0	482.6
Space group	<i>Pnma</i>	<i>Cmcm</i>	<i>Cmcm</i>	<i>Cmcm</i>	<i>Cmcm</i>	<i>Cmcm</i>	<i>Cmcm</i>
a (Å)	11.8648(3)	9.2028(4)	9.3242(3)	9.3870(4)	9.4083(3)	9.4738(2)	9.5885(2)
b (Å)	5.47187(9)	11.7954(5)	11.8173(5)	11.8152(5)	11.8342(4)	11.8412(3)	11.8475(3)
c (Å)	9.1775(2)	5.5238(2)	5.6091(2)	5.6320(2)	5.6413(1)	5.6579(1)	5.6785(1)
Cell volume (Å ³)	595.83(2)	599.62(4)	618.04(4)	624.64(4)	628.09(3)	634.71(2)	645.07(2)
$F(000)$	191.65	191.79	192.14	192.28	192.35	192.49	192.63
Calculated density (g/cm ³)	5.415	5.375	5.203	5.144	5.113	5.055	4.969
Number of parameters	30	23	23	23	23	23	23
Excluded regions in 2θ (deg.)	—	—	—	—	—	41.9–43.2	24.5–25.3; 42.2–42.9; 47.8–48.7
No. of observed reflections	199	110	112	115	115	117	118
R_p (%)	14.2	15.4	15.0	14.7	15.2	13.2	12.7
R_{wp} (%)	15.4	17.4	16.4	15.5	15.8	14.0	14.1
R_{exp} (%)	3.72	3.78	4.13	4.42	3.89	3.96	4.53
χ^2	17.1	21.2	15.8	12.3	16.5	12.4	9.75

whereas weak anomaly could be seen around $x = 0.05$, which may be related to the structural phase transition. Figures 3(c), 3(d) show temperature dependence of local structure parameters for $x = 0.05$. Although $x = 0.05$ is *Pnma*, being the same as BaFe_2Se_3 , there is no enhancement of ladder distortion. Figures 3(e), 3(f) show T dependence of local structure parameters for $x = 0.75$. Change in local structure was detected around $T = 120$ and 70 K, where two successive magnetic phase transitions were observed from the paramagnetism to stripe-II, and from the stripe-II to stripe-I, respectively (described in III C).

B. BULK PROPERTIES

Temperature dependence of electrical resistivity (ρ) along the leg direction is shown in Fig. 4(a). No anomaly was seen in ρ in the whole measured temperature range. Intermediate compounds show much lower ρ than that of the parent compounds; at $x = 0.55$, ρ at 300 K shows the lowest value $\rho = 1.89 \times 10^{-2} \Omega \text{ cm}$, which is 10^2 times smaller than that of BaFe_2Se_3 and 10^5 smaller than that of CsFe_2Se_3 . The temperature dependence of ρ shows one-dimensional variable-range-hopping (VRH) behavior in low- T region, given by $\rho \propto \exp[(T_0/T)^{1/2}]$ [Fig. 4(b)] [31–33]. It is known that $(k_B T_0)^{-1}$ of 1D VRH is proportional to the localization length and the density of states at Fermi level. Figure 5 shows the $(k_B T_0)^{-1}$ obtained by fitting the data for $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ versus x . Although ρ of CsFe_2Se_3 ($x = 1$) [25] are deviated from the 1D VRH behavior, we fit it with 1D VRH to compare $(k_B T_0)^{-1}$ with those of $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$. Interestingly,

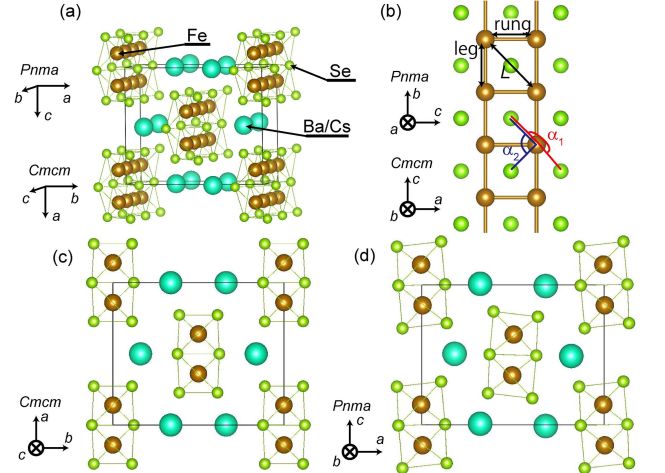


FIG. 2. (color online). (a), (b) Crystal structures of $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$. A cuboid with solid lines indicates a crystallographic unit cell. Note that the definition of a , b and c axis is different from each other for the *Pnma* and *Cmcm* structures. Distinction for arrangement of ladder between (c) *Cmcm* and (d) *Pnma* space group. In *Pnma*, ladders are slightly tilted toward the a axis.

the largest $(k_B T_0)^{-1}$ was observed for $x = 0.65$, which is closer to the strong insulator CsFe_2Se_3 than BaFe_2Se_3 .

Figure 4(c) shows specific heat (C_p) as a function of temperature. No anomaly was observed in all measured temperature and all x ranges. The C_p/T versus T^2 plots at low temperature indicate T -linear contribution (γ term) extrapolated as $T \rightarrow 0$ except for $x = 0.15$ [Fig. 4(d)]. This suggests that $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ have

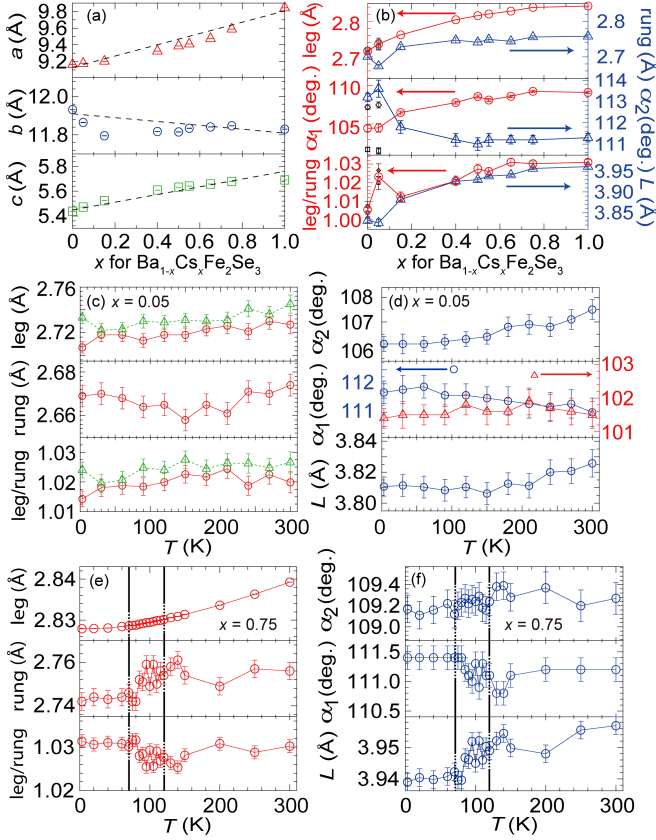


FIG. 3. (color online). (a) Cs concentration (x) dependence of lattice constants at 300 K. The data for $x = 0$ and 0.05 are converted into the definition of $Cmcm$ symmetry. The dashed lines represent linear fit to the lattice constants. (b) The x dependence of the Fe-Fe bond length along the leg and rung direction; Se-Fe-Se bond angle α_1 and α_2 ; the ratio between the bond length along the leg and rung direction, and the diagonal Fe-Fe bond length (L) [see Fig. 2(b)]. (c), (d) T dependence of local structures for $x = 0.05$. Note that two distinct values for leg, leg/rung and α_1 are owing to $Pnma$ space group (black square and rhomboid). The red circles show the average of the two values. (e), (f) T dependence of local structures for $x = 0.75$. Black lines indicate magnetic transition temperatures (see in text).

finite γ values. As discussed below, magnetization measurements indicate that the samples contain Fe_7Se_8 . One can suspect that the obtained specific heat contain the contribution from the impurity. However, the amount of Fe_7Se_8 is at most 1 % molar ratio (see below) and its γ values are relatively small; 8 and 4.4 mJ/mol K^2 for $4c$ and $3c$ structures of Fe_7Se_8 , respectively [34, 35]. Therefore the impurity effect is negligible. The γ values obtained by linear fit for $T < 3.3$ K [solid lines in Fig. 4(d)] are summarized in Fig. 5. We note that $(k_B T_0)^{-1}$ and γ show a similar x dependence.

Figure 6 shows the magnetic susceptibilities (χ) defined as magnetization (M) over magnetic field (H), that is, $\chi \equiv M/H$, for single crystals of $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ under $H = 50000$ Oe. The samples contain a tiny amount

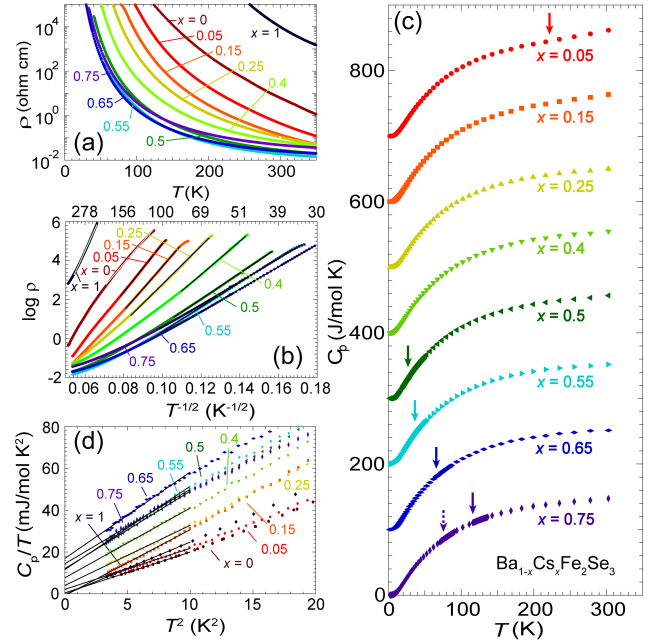


FIG. 4. (color online). (a) Temperature dependence of electrical resistivity of $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ along the leg direction. (b) One-dimensional variable range hopping type plot of (a). Solid lines indicate the results of fitting. (c) Temperature dependence of the specific heat (C_p). Arrows show the magnetic transition temperature. Note that each data shifted by 100 $T/\text{mol K}$ for clarity. (d) Specific heat divided by temperature against T^2 type plot. Solid lines indicate the results of fitting. Although $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ show an insulating behavior, γ term (T -linear term) remains.

of ferromagnetic impurity, and in this case, Fe_7Se_8 is the most plausible one. Estimated molar ratio of Fe_7Se_8 in $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ from hysteresis loop is less than 1 % for $x = 0.05$, and 0.5 % for other compositions [36]. We also measured the temperature dependence of magnetization for the annealed Fe_7Se_8 between $T = 2$ and 300 K on field cool (FC) and zero-field cool (ZFC) measurements [inset of Fig. 6], and found that χ decreases below 120 K on cooling. However χ of $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ do not show such behavior, indicating that the negligible contribution from Fe_7Se_8 impurity phase. The χ of $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ show paramagnetic increase as temperature decreases, and glassy behaviors were observed for $0.05 \leq x \leq 0.4$ at low temperatures. The systematic decrease of the spin-glass transition temperature (T_f) implies that this behavior is of intrinsic nature; if this behavior were due to ferromagnetic impurity phase, T_f would be constant.

C. MAGNETIC STRUCTURES

To elucidate variation of magnetic structures in $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$, we performed powder neutron diffraction measurements. Figures 7, 8 and 9 show the powder diffraction patterns of several temperatures from 3 to 300

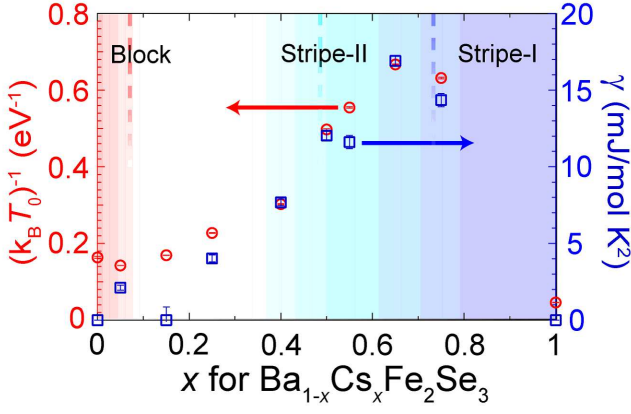


FIG. 5. (color online). Cs concentration (x) dependence of γ (left-axis) and $(k_B T_0)^{-1}$ (see text, right-axis). They show similar behavior and take the maximum value for $x = 0.65$. In background, the type of magnetism at low temperature is shown.

K, in a selected scattering wave vector Q range. For $x = 0.05, 0.4, 0.65$ and 0.75 the diffraction patterns were collected using ECHIDNA, and for $x = 0.15, 0.25, 0.5$ and 0.55 using WAND.

1. $0 < x \leq 0.15$

The diffraction patterns for $x = 0.05$ and 0.15 are shown in Fig. 7. For $x = 0.05$ magnetic reflection appears at $Q \sim 0.7 \text{ \AA}^{-1}$, which corresponds to the main peak of block magnetism in BaFe_2Se_3 appearing at the magnetic wave vector $\mathbf{q}_m = (0.5, 0.5, 0.5)$ [20]. This magnetic scattering appears below $T^* = 290(10) \text{ K}$, and grows with decreasing temperature. This peak is broadened beyond instrumental resolution even at the lowest temperature, suggesting that only 5 % doping eliminates the long ranged correlation of the block magnetism. Likewise, for $x = 0.15$, only magnetic diffuse scattering was observed below $T^* = 215(15) \text{ K}$ at similar position to the block magnetism. The correlation length is roughly estimated from the peak width as: $16(4) \text{ \AA}$ for $x = 0.05$ at 3 K , $9(3) \text{ \AA}$ for $x = 0.15$ at 3.4 K . BaFe_2Se_3 ($x = 0$) have $19(5) \text{ \AA}$ correlation length at 275 K [20], thus these correlation lengths seem to decrease toward $x = 0.25$, where the magnetic orders are completely suppressed.

2. $0.4 \leq x < 1$

Figure 9 shows diffraction patterns for $0.4 \leq x < 1$, showing stripe magnetism. We first focus on $x = 0.75$. On cooling, a magnetic diffuse scattering develops below 250 K at $Q = 1.2 \text{ \AA}^{-1}$. In contrast to the block magnetism, magnetic reflections become almost resolution limited below $130(5) \text{ K}$. These magnetic reflections

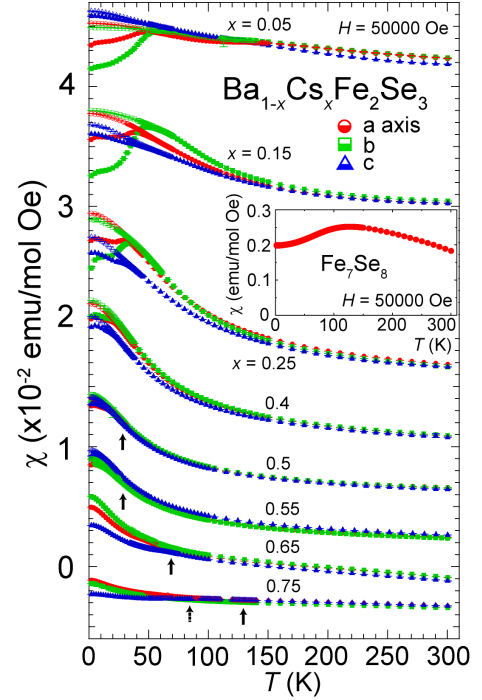


FIG. 6. (color online). Temperature (T) dependence of magnetic susceptibility (χ) for $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ along the a, b and c axis in the $Cmcm$ notation at the magnetic field $H = 50000 \text{ Oe}$. The solid and open symbols indicate zero-field cooled (ZFC) and field cooled (FC) measurements, respectively. Note that each data are shifted for clarity. The arrows indicate the magnetic transition temperatures. The inset shows temperature dependence of χ for the magnetic impurity Fe_7Se_8 .

change their positions below $80(5) \text{ K}$, which corresponds to additional magnetic transition [inset in Fig. 10(a)].

All the magnetic peak positions below $80(5) \text{ K}$ are well accounted for by the propagation vector $\mathbf{q}_m = (0.5, 0.5, 0)$, which is the same as CsFe_2Se_3 . To identify this magnetic structure, we applied representation analysis and performed Rietveld analysis. Basis vectors (BVs) of the irreducible representations (irreps) of \mathbf{q}_m were calculated using the SARA h code [37]. The obtained BVs are listed in Table II in Ref. [25]. We sorted all BVs by comparing R -factors and found that ψ_9 , with spins aligned along the leg direction, has the best fit with $R_p = 11.7 \%$; the second best is 12.8% for ψ_2 . The Rietveld refinement results are shown in Fig. 10(a). The obtained magnetic structure is shown in Fig. 11(b). We call this magnetic structure as stripe-I magnetism. This magnetic structure is completely the same as that of CsFe_2Se_3 , implying the relatively stable stripe-I magnetism against the Ba substitution.

On the other hand, between $130(5)$ and $80(5) \text{ K}$ magnetic reflection positions cannot be accounted for by the propagation vector of BaFe_2Se_3 , $\mathbf{q}_m = (0.5, 0.5, 0.5)$ nor of CsFe_2Se_3 , $\mathbf{q}_m = (0.5, 0.5, 0)$. The peak positions are instead well accounted for by $\mathbf{q}_m = (0.5, 0, 0)$, however

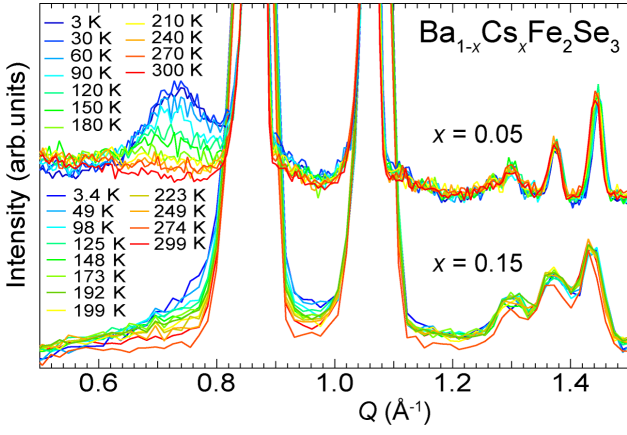


FIG. 7. (color online). Powder neutron diffraction patterns for $x = 0.05$ and 0.15 taken at several temperature points. The data were collected at the listed temperatures using ECHIDNA for $x = 0.05$ and WAND for $x = 0.15$.

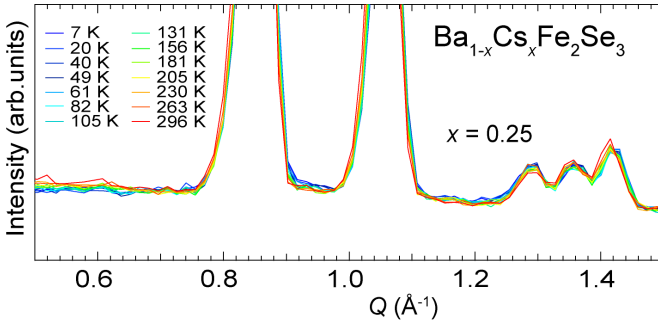


FIG. 8. (color online). Powder neutron diffraction patterns for $x = 0.25$ taken at several temperature points. The data were collected at the listed temperatures using WAND.

peak intensities of the magnetic reflections are too weak to perform Rietveld refinements. With decreasing x , we found that the new magnetic phase becomes the ground states in $x = 0.5, 0.55$ and 0.65 above 3 K and that the reflections are the most intense for $x = 0.65$. Therefore we analyzed the magnetic structure for $x = 0.65$. Figure 10(c) shows a diffraction pattern for $x = 0.65$ taken at 3 K and a result of Rietveld refinement. We performed representation analysis in the same way as $x = 0.75$ and obtained BVs summarized in Table IV. The sites of Fe atom in orbit 1 and orbit 2 cannot be exchanged by symmetry operations that leave the \mathbf{q}_m invariant. Therefore, we can choose different phase factors of moments for Fe atoms in orbit 1 and orbit 2. Magnetic moment of the j -th Fe atom \mathbf{m}_j ($j = 1, 2 \in \text{orbit1}$ or $j = 3, 4 \in \text{orbit2}$) is given by the real part of $\mathbf{m}_{j \in \text{orbit1}} = C\psi_1^{j \in \text{orbit1}} e^{i\phi_1} e^{2\pi i \mathbf{q}_m \cdot \mathbf{t}}$ or $\mathbf{m}_{j \in \text{orbit2}} = C\psi_1^{j \in \text{orbit2}} e^{i\phi_2} e^{2\pi i \mathbf{q}_m \cdot \mathbf{t}}$, where $\psi_1^{j \in \text{orbit } i}$ means BV ψ_1 for j -th Fe atom belongs to orbit i ($i = 1, 2$), ϕ_i is phase factor of orbit i , \mathbf{t} is the lattice translation vector and C is a real constant. We assumed that orbit 1 and orbit 2 are in the same irreps and that all

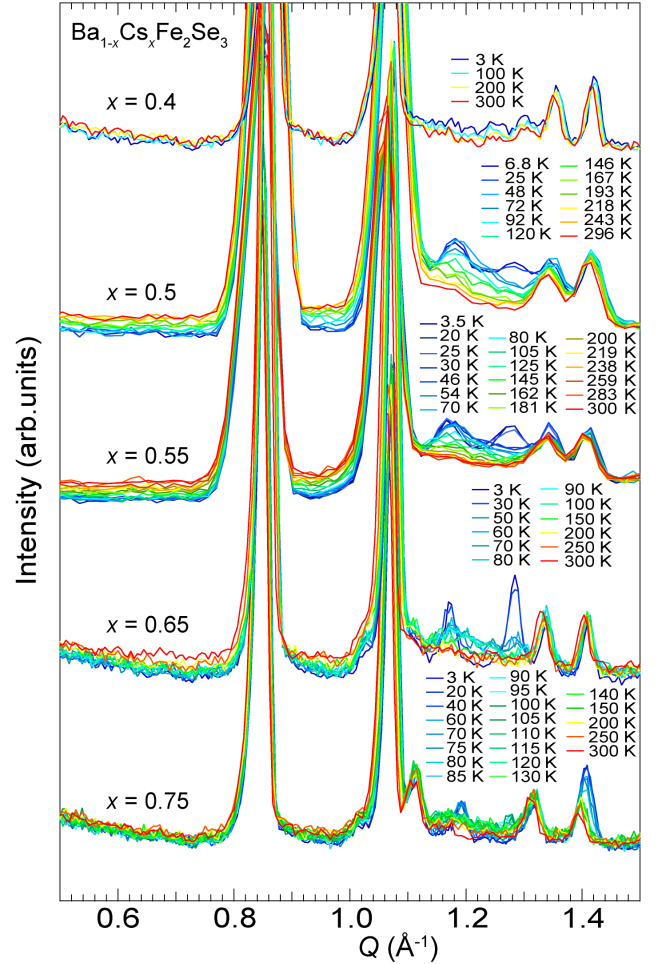


FIG. 9. (color online). Powder neutron diffraction patterns for $x = 0.4$ taken at several temperature points, $0.5, 0.55, 0.65$, and 0.75 . The data were collected at the listed temperatures using ECHIDNA for $x = 0.4, 0.65$ and 0.75 , and using WAND for $x = 0.5$ and 0.55 .

Fe atoms have the same moment size, because Fe atoms in paramagnetic state are in single site (see Table II). The best fit is a combination of ψ_1 with the phase factor $\phi_1 = 5\pi/4$ and $\phi_2 = \pi/4$, where $R_p = 12.0\%$ (the second best is 12.2% for ψ_5).

The schematic magnetic structure is shown in Fig. 12(c). We call this magnetic structure as stripe-II. Stripe-I and stripe-II have similar intra-ladder structure, where magnetic moments are arranged to form ferromagnetic units along the rung direction, and the units stack antiferromagnetically along the leg direction. In contrast, the spin directions [Fig. 11(b) and 11(c)] and the inter-ladder relation [Fig. 11(d) and 11(e)] are different between stripe-I and stripe-II.

Knowing the magnetic structure of the $x = 0.65$ sample, we tried to determine the magnetic structure for $x = 0.75$ at 90 K, where the same initial magnetic structure is assumed. The best fits are obtained for ψ_4 and ψ_5 with $R_p = 11.7\%$, however ψ_1 have the close value with

TABLE IV. Basis vectors (BVs) of irreducible representations (irreps) for the space group $Cmcm$ with the magnetic wave vector $\mathbf{q}_m = (0.5, 0, 0)$. Subscripts show the moment direction. Columns for positions represent No.1: $(x, 1/2, 0)$, No. 2: $(x, 1/2, 1/2)$, No. 3: $(1-x, 1/2, 1/2)$ and No. 4: $(1-x, 1/2, 0)$.

Irreps	BV	Orbit 1		Orbit 2	
		No. 1	No. 2	No. 3	No. 4
Γ_1	ψ_1	2_a	-2_a	2_a	-2_a
Γ_2	ψ_2	2_a	2_a	2_a	2_a
Γ_3	ψ_3	2_b	2_b	2_b	2_b
	ψ_4	2_c	-2_c	2_c	-2_c
Γ_4	ψ_5	2_b	-2_b	2_b	-2_b
	ψ_6	2_c	2_c	2_c	2_c

$R_p = 11.8\%$. The χ [Fig. 6(b)] show little anisotropy for $0.5 \leq x \leq 0.75$. Nevertheless it is hard to expect any anisotropic change without variations in significant structural parameter for $x = 0.65$ and $x = 0.75$, we speculate that the spin orientation is parallel (ψ_1) also at 90 K of the $x = 0.75$ sample. To confirm this orientation, single crystal neutron diffraction measurements is desired.

For $0.4 \leq x \leq 0.75$, magnetic diffuse scatterings were also observed at $Q \sim 1.2 \text{ \AA}^{-1}$ at higher temperatures. These scatterings evolve below $\sim 200\text{K}$ [see rhomboids in Fig. 13]. The positions are different from that of the $x = 0.05$ and 0.15 samples, where diffuse scatterings appear at $Q \sim 0.7 \text{ \AA}^{-1}$ near the Bragg reflection position of the block magnetism. Therefore these diffuse scatterings would reflect stripe-type short-range correlation. No diffuse scattering was observed in CsFe_2Se_3 .

3. Magnetism of $x = 0.25$

Interestingly, for $x = 0.25$, no magnetic reflection was observed down to 7 K as shown in Fig. 8. The χ for $x = 0.25$ shows the spin-glass behavior, and it is consistent with this result. Note that other intermediate compounds ($0.05 \leq x \leq 0.4$) also show spin-glass behavior, however they have some magnetic scatterings (mostly diffuse) in powder neutron diffraction.

4. Moment size of $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$

Temperature dependence of estimated magnetic moment sizes for several x are shown in Fig. 12. The moment sizes of $x = 0.65$ and 0.75 are the results of Rietveld refinement. For $x = 0.5$ and 0.55 moment sizes were obtained from comparing between integrated intensity of the 021_{Cmcm} nuclear peak and the $\frac{1}{2}21_{Cmcm}$ magnetic peak. The $x = 0.75$ sample shows successive phase transitions. Around 130 K the stripe-II magnetism appears and the magnetic moment grows to $0.31(3) \mu_B$. In 85 - 95 K, the stripe-I and stripe-II structures could coexist, because in this temperature range the moment size of

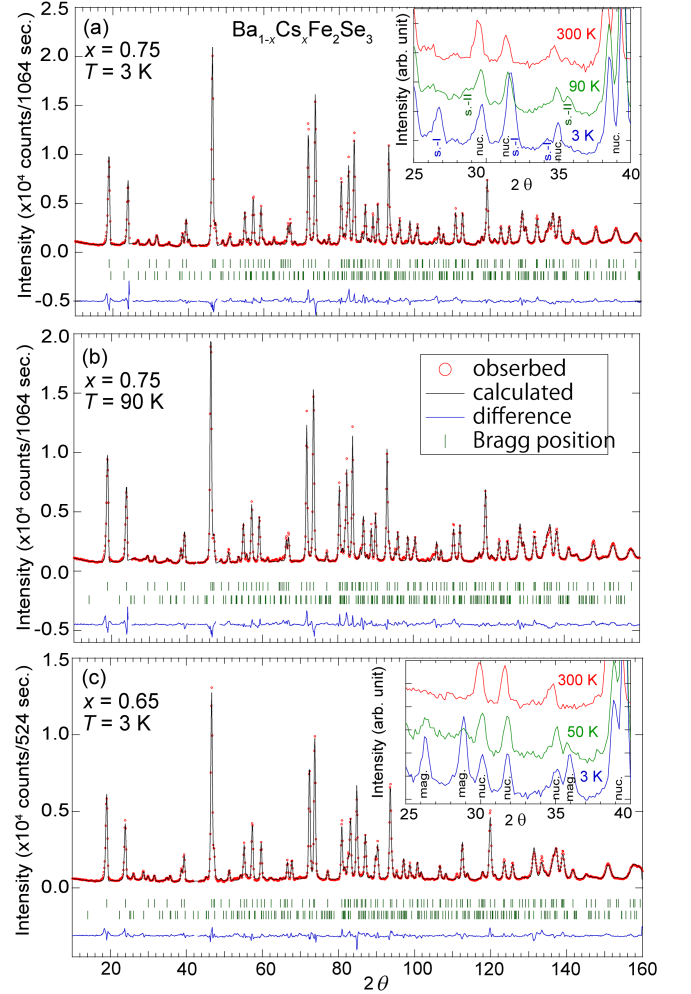


FIG. 10. (color online). High-resolution powder neutron diffraction patterns for (a) $x = 0.75$ at 3 K, (b) $x = 0.75$ at 90 K, and (c) $x = 0.65$ at 3 K using ECHIDNA with Rietveld analysis results (solid lines). The calculated positions of nuclear and magnetic reflections are indicated (green ticks). The bottom line gives the difference. The insets show (a) change of positions of magnetic reflections from stripe-II to stripe-I magnetism and (c) temperature evolution of magnetic reflections for $x = 0.65$.

stripe-II becomes small. On further cooling, the stripe-I magnetism is finally stabilized, and the magnetic moment reaches to $2.01(5) \mu_B$ at 3 K. The $x = 0.5, 0.55$ and 0.65 samples, where stripe-II magnetism appears, show similar moment size to the $x = 0.75$ sample at the lowest temperature; $0.39(3) \mu_B$ for $x = 0.5$; $0.55(3) \mu_B$ for $x = 0.55$; and $0.60(2) \mu_B$ for $x = 0.65$. As x decreases to the region where magnetism is suppressed, the moment size decreases.

In iron-based SCs, magnetic structure shows a close correlation with the ordered moment. Single-stripe magnetism usually has an ordered moment smaller than $1 \mu_B$, double-stripe has $\sim 2 \mu_B$ and block magnetism has a larger moment around $3 \mu_B$. On the other hand for

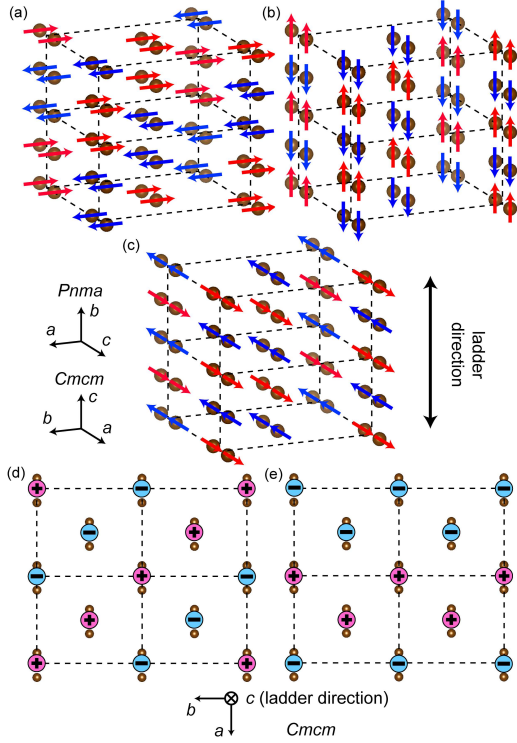


FIG. 11. (color online). The schematic figures of magnetic structures for: (a) block magnetism (b) stripe-I magnetism, and (c) stripe-II magnetism. The inter-ladder relation of spins are shown in (d) stripe-I and (e) stripe-II magnetism. The + and - sign indicate ferromagnetic and antiferromagnetic correlation in neighboring ladders, respectively.

iron-based ladder compounds, stripe-II magnetism has $\sim 0.5 \mu_B$, stripe-I has $\sim 2 \mu_B$ and block magnetism has $\sim 3 \mu_B$. The correlations are basically consistent between the 2D iron-based SCs and the ladder compounds. It may be noteworthy that the ladder compounds cover whole range of the moment size seen in iron-based SCs.

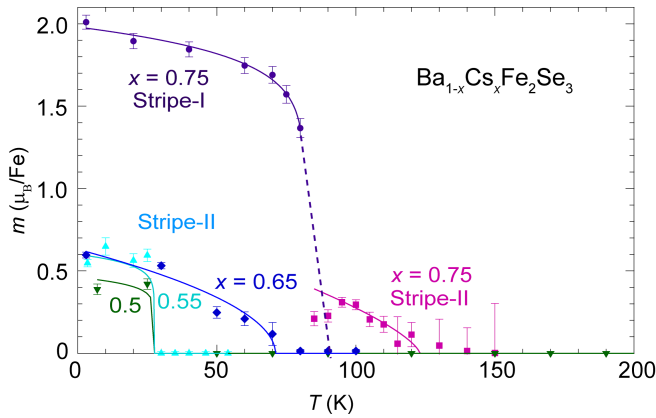


FIG. 12. (color online). Temperature dependence of estimated magnetic moment. The data of $x = 0.65$ and 0.75 were collected using ECHIDNA, and of $x = 0.5$ and 0.55 using WAND.

5. Magnetic phase diagram

Figure 13 shows established temperature and composition phase diagram of $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$. Interestingly, T_N is drastically suppressed by increasing x , and only 5 % Cs doping (*i.e.* $x = 0.05$) destabilizes the long range order of the block magnetism. Almost simultaneously, space group changes from $Pnma$ to the $Cmcm$ between $x = 0.05$ and 0.15 . Compared with the block magnetism, stripe-I and II magnetism can be seen in a large region of phase diagram and are relatively resilient the Cs doping. For $x = 0.75$, successive magnetic phase transition from the paramagnetic state to stripe-II and from stripe-II to stripe-I was observed. With decreasing Cs concentration x , the stripe-II magnetism becomes ground state for $0.5 \leq x \leq 0.65$ and T_N decreases gradually. The long range magnetic order is completely suppressed at $x = 0.4$.

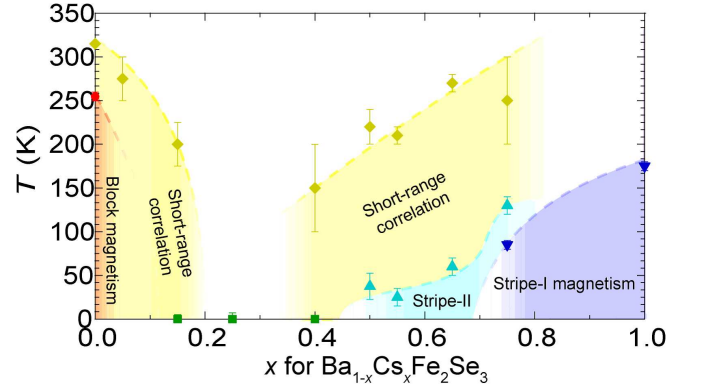


FIG. 13. (color online). Magnetic phase diagram determined by the powder neutron diffraction. The data were collected down to 3 K ($x = 0.05, 0.4, 0.65$, and 0.75), 5 K ($x = 0.15, 0.5$ and 0.55), and 7 K ($x = 0.25$). Rhomboids indicate the temperature where diffuse scattering appears. Squares, upward triangles, and downward triangles indicate the magnetic phase transition temperature of the block, stripe-I, and stripe-II magnetism, respectively.

IV. DISCUSSION

We here discuss the interplay of crystal structure, bulk properties, and magnetism of $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$.

The T -linear contribution (γ value) of C_p becomes large around $x = 0.65$ (Fig. 5). Possible origin of finite γ values in C_p may be spin-glass state, magnons or electrons.

Firstly, for the spin-glass possibility, we obtained the highest T_f for $x = 0.15$, and for $0.5 \leq x \leq 0.75$ glassy behavior did not appear [Fig. 6(b)]. This is not consistent with the behavior of γ values, thus the possibility of spin-glass contribution can be excluded.

Secondly, temperature dependence of C_p is known as

$C_p \propto T^{d/\nu}$ for magnetic excitations associated with magnons, where d is spatial dimensionality, $\nu = 1$ for antiferromagnetic; $= 2$ for ferromagnetic ordered system. Thus T -linear contribution of the magnons could be due to 1D antiferro-type or 2D ferro-type. The former is plausible, and the latter should be unlikely due to antiferromagnetic structure of $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$. In stripe-II magnetism region, ordered magnetic moments are smaller than that of parent compounds and thus fluctuating moment may be significant. This part may contribute to the larger γ value in the stripe-II region. However, the parent compounds, which have larger moment size than intermediate compounds, do not show finite γ values. Therefore it would be difficult to conclude that the contribution of magnon is dominant.

Finally, for the case of electronic specific heat, electrons may have density of states at Fermi level, but random potential prevents their itinerancy. In this possibility, the resistivity would follow the VRH model in low temperatures, and the magnetic moment would reduce because of its itinerancy. This is consistent with the fact that similar fashion is seen in the γ values and $(k_B T_0)^{-1}$. The small moments of stripe-II magnetism is also consistent with this scenario. These behaviors can be seen in insulating amorphous alloys, however theoretical model to account for γ in insulating system is still controversial [38]. We suggest that this is the most plausible scenario among these possibilities.

The obtained results indicate the close relation between the crystal and magnetic structures. In the $Pnma$ structure, the intra-ladder structure is distorted and rungs are slightly tilted from the parallel alignment along the rung direction [Fig. 2(d)]. It is reported that BaFe_2Se_3 shows enhancements of distortion in intra-ladder structure below $T_N \sim 255$ K, and this indicates magnetoelastic coupling [20, 23]. On the other hand, at $x = 0.05$, where only magnetic diffuse scattering was observed, there is no drastic intra-ladder distortion in measured temperature range [Fig. 3(c), 3(d)]. In addition, at $x = 0.15$ where the crystal structure has the $Cmcm$ space group, only weaker magnetic diffuse scattering than that of $x = 0.05$ was observed. These facts suggest that no long range order of the block magnetism can exist in the $Cmcm$ structure, and that the block magnetism may be sensitive to the distortion of intra- and inter-ladder atom arrangement.

The stripe-I and II magnetism are more resilient than the block magnetism to the elemental substitution for $0.4 \leq x \leq 0.75$ region. No structure transition was observed in $0.4 \leq x \leq 0.75$. The stability of the magnetic structure would be due to that of the crystal structure.

For $x = 0.75$, the local structure changes slightly at the transition temperatures [Fig. 3(e), 3(f)]. However the relation between the crystal and the magnetic structure is unclear at present.

Next we focus on the $x = 0.25$ sample, where no diffuse or long range magnetic scattering observed by powder neutron diffraction measurements down to 7 K. In

this case, moments would vanish or freeze without long range order nor short range correlation. From susceptibility measurements, the moments seem to remain finite [Fig. 6(b)]. Hence, there must be fluctuating moment (or glassy component) even at the lowest temperature. This compound has the competitions of block and stripe-II magnetism, as well as the $Pnma$ and $Cmcm$ structure. The suppression of magnetism for $x = 0.25$ would be due to these instabilities.

We now compare obtained magnetic phase diagram (Fig. 13) with theoretical calculations based on a five-orbital Hubbard model in a finite size Fe-Se two-leg-ladder [39]. The calculations correspond to formal valences of Fe^{2+} (correspond to BaFe_2Se_3 , or $x = 0$) and $\text{Fe}^{2.25+}$ ($\text{Ba}_{0.5}\text{Cs}_{0.5}\text{Fe}_2\text{Se}_3$, or $x = 0.5$). They took account of the lattice distortion seen in the $Pnma$ space group as anisotropic hopping parameters, and they calculated the $x = 0.5$ sample as the $Pnma$ (experimental results indicate $x = 0.5$ is $Cmcm$). Block and CX structure [corresponds to stripe-I and II magnetism, see Fig. 1 in Ref. [39]] are stable in a robust region of their phase diagrams for Fe^{2+} and $\text{Fe}^{2.25+}$, respectively. Except for the orientation of spins, their results are basically consistent with our findings. Interestingly, the stripe magnetism can be stabilized in the $Pnma$ space group. Hence the theory suggests that the stability of stripe-I and II magnetism are due to not only that of crystal structure but also that of electronic structure. Note that magnetic structures obtained by our study are realized in the realistic ratio $J_H/U = 0.25$ and $U/W \sim 0.5$ [see in Ref. [39]]. This implies $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ would be "intermediate" coupling compounds [5].

Pressure-induced superconductivity was reported in cuprate ladder compounds $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ [40–42]. This compound has Cu_2O_3 combined two-leg-ladder structure, and is insulator. Their resistivity becomes lower with increasing pressure and show superconductivity at 3 GPa. Moreover, the suppression of magnetism provides superconductivity in 2D iron-based SCs, and we discovered that the magnetism of $\text{Ba}_{0.75}\text{Cs}_{0.25}\text{Fe}_2\text{Se}_3$ ($x = 0.25$) is completely suppressed. Therefore applying pressure for this composition may be an intriguing way to pursue superconductivity in future. Pressure-effect study is now in progress.

V. CONCLUSION

We performed a comprehensive study on the interplay of crystal structure, bulk properties, and magnetism for $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ by electrical resistivity, specific heat, magnetic susceptibility, X-ray diffraction and powder neutron diffraction measurements. The space group changes from $Pnma$ to $Cmcm$ between $x = 0.05$ and 0.15 , where block magnetism is drastically suppressed concomitantly. New type of magnetic structure, stripe-II, appeared where T -linear term of C_p is finite. For $x = 0.75$ we observed successive phase transitions from stripe-II to

stripe-I with a slight structure distortion. Typical magnetic moment sizes in $\text{Ba}_{1-x}\text{Cs}_x\text{Fe}_2\text{Se}_3$ was determined as: stripe-II magnetism $\sim 0.5\mu_B$; stripe-I $\sim 2\mu_B$; and block magnetism $\lesssim 3\mu_B$. They cover the moment size range seen in the all iron-based SCs: single-stripe magnetism $< 1\mu_B$; double-stripe $\sim 2\mu_B$; and block magnetism $\sim 3\mu_B$. Notably, there is no diffuse nor resolution-limited magnetic scattering in powder neutron diffraction pattern down to 7 K for $x = 0.25$, where competition of the block and the stripe-II magnetism and of the $Pnma$ and $Cmcm$ structure is expected.

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